Electronic Supplementary Material (ESI) for RSC Advances.

Electronic and Magnetic Properties Regulation of Finite to Infinite Half Sandwich Organo-Transition-Metal-Complexes Functionalized Graphene

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Supporting Information

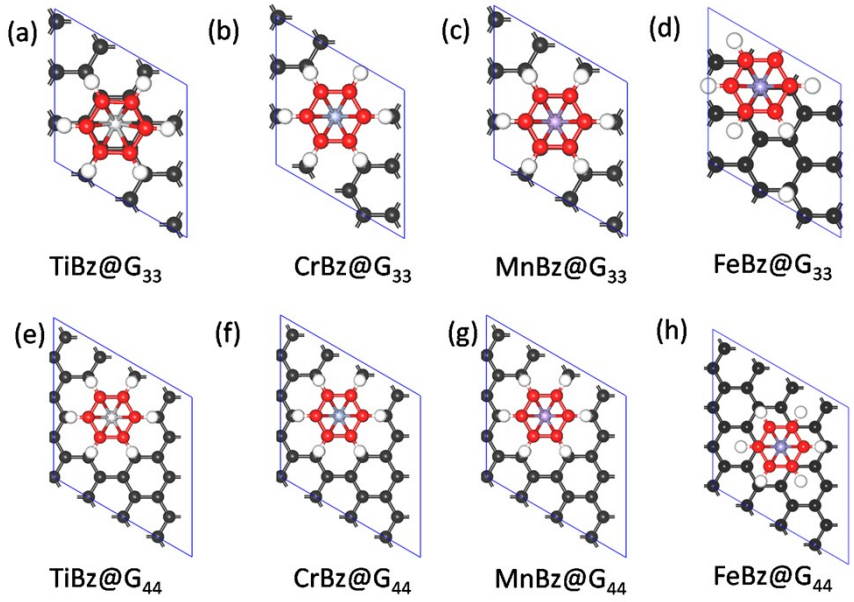


Figure S1. Optimized Structures of $TMBz@G_{33}$ and $TMBz@G_{44}$.

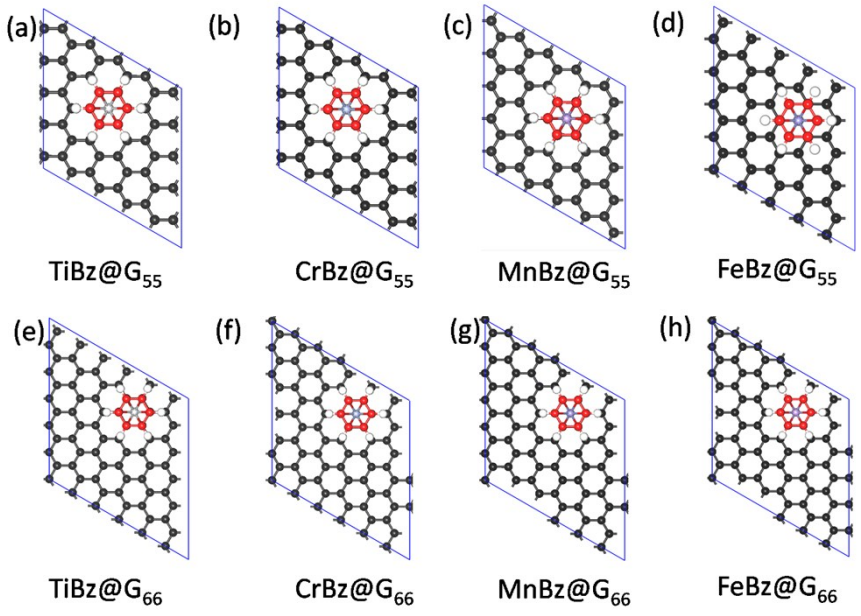
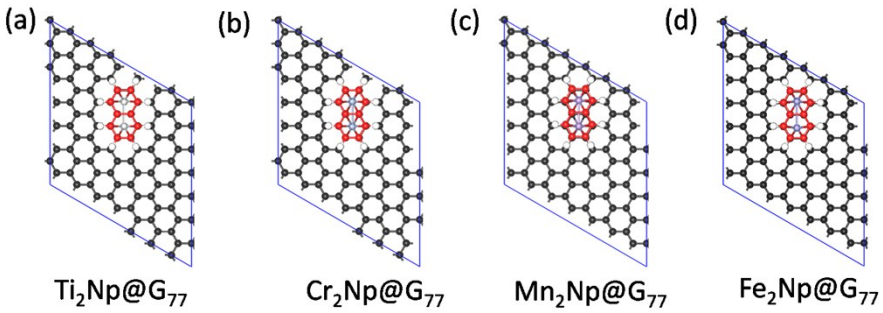


Figure S2. Optimized Structures of TMBz@G_{55} and TMBz@G_{66}.



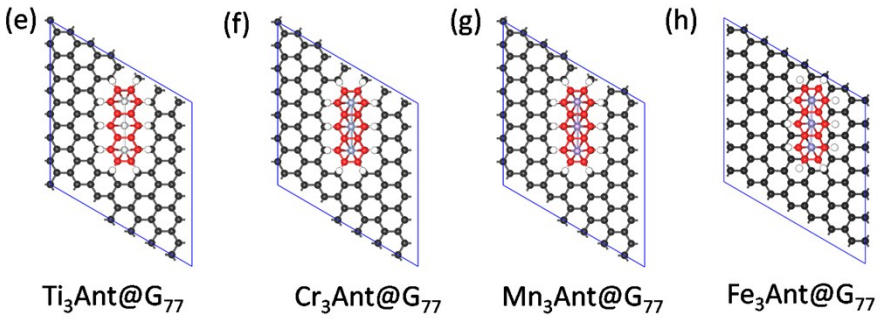


Figure S3. Optimized Structures of $TM_2Np@G_{77}$ and $TM_3Ant@G_{77}$.

Table S1. The systems with finite adsorbed molecule (Sys), the C-C bond length of organic ligands ($L_{C\text{-}C(OL)}$) and of graphene ($L_{C\text{-}C(G)}$), the C-H bond lengths of organic ligands ($L_{C\text{-}H}$), the distance of TM atom to the geometric center of organic molecules ($D_{TM\text{-}OM}$) and graphene plane ($D_{TM\text{-}G}$), and the distance of TM-TM ($D_{TM\text{-}TM}$) atoms in FTML@SLGs system.

Sys	TM	$L_{C\text{-}C(OL)}$(Å)	$L_{C\text{-}C(G)}$(Å)	$L_{C\text{-}H}$(Å)	$D_{TM\text{-}OM}$(Å)	$D_{TM\text{-}G}$(Å)	$D_{TM\text{-}TM}$(Å)
TMBz@G_{33}	Ti	1.428-1.431	1.414-1.442	1.089	1.740	1.871	
	Cr	1.420	1.414-1.441	1.092	1.609	1.684	
	Mn	1.420,1.421	1.420-1.434	1.091	1.537	1.708	
	Fe	1.419,1.420	1.421-1.433	1.092	1.560	2.037	
TMBz@G_{44}	Ti	1.426-1.430	1.417-1.439	1.090	1.749	1.730	
	Cr	1.423	1.417-1.436	1.091	1.589	1.687	
	Mn	1.421	1.417-1.436	1.091	1.543	1.677	
	Fe	1.419,1.420	1.421-1.434	1.091	1.562	2.036	
TMBz@G_{55}	Ti	1.429,1.430	1.418-1.440	1.091	1.736	1.824	
	Cr	1.423,1.424	1.418-1.435	1.091	1.590	1.692	
	Mn	1.420,1.421	1.418-1.435	1.090	1.544	1.677	
	Fe	1.419	1.422-1.434	1.091	1.621	1.793	
TMBz@G_{66}	Ti	1.425-1.428	1.418-1.441	1.090	1.755	1.824	
	Cr	1.422	1.417-1.438	1.091	1.596	1.691	
	M	1.419,1.420	1.420-1.436	1.091	1.543	1.684	

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	Fe	1.417-1.419	1.422-1.435	1.091	1.561	2.031	
$TM_2Np@G_{77}$	Ti	1.406-1.470	1.418-1.447	1.090	1.796,1.796	1.898,1.898	2.604
	Cr	1.411-1.455	1.418-1.441	1.091	1.672,1.672	1.756,1.756	2.626
	Mn	1.414-1.452	1.416-1.444	1.092	1.584,1.700	1.762,1.633	2.735
	Fe	1.418-1.467	1.415-1.448	1.091	1.640,1.678	1.755,1.703	2.822
$TM_3Ant@G_{77}$	Ti	1.408-1.452	1.418-1.446	1.090	1.831,1.823, 1.831	1.898,1.894,1.898	2.561,2.557
	Cr	1.412-1.452	1.416-1.446	1.091	1.685,1.703, 1.685	1.740,1.822,1.787	2.521,2.524
	Mn	1.414-1.449	1.418-1.437	1.092	1.633,1.709, 1.645	1.719,1.730,1.709	2.596,2.601
	Fe	1.421-1.454	1.425-1.444	1.093	1.669,1.734, 1.675	2.038,2.028,2.042	2.443,2.513

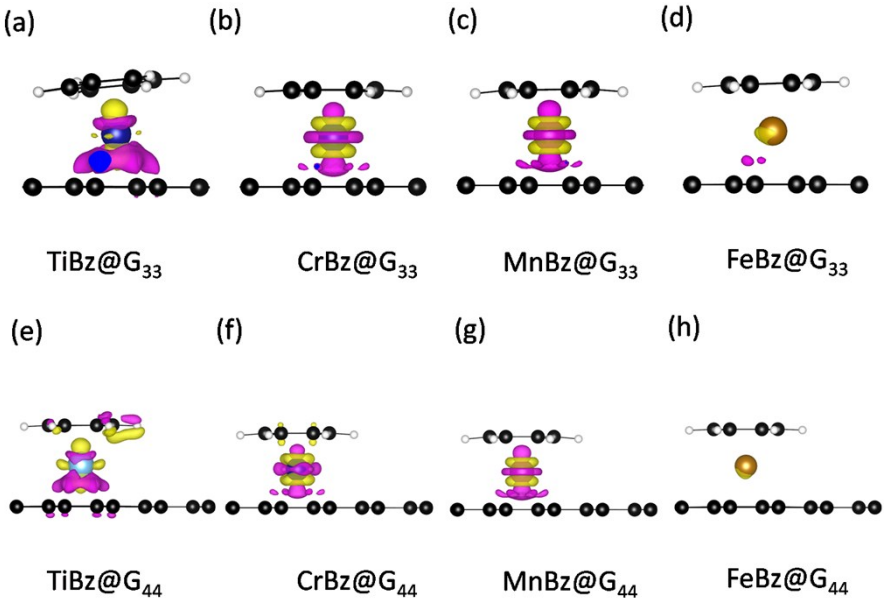

Figure S4.The charge density differences of $TMBz@G_{33}$ and $TMBz@G_{44}$.

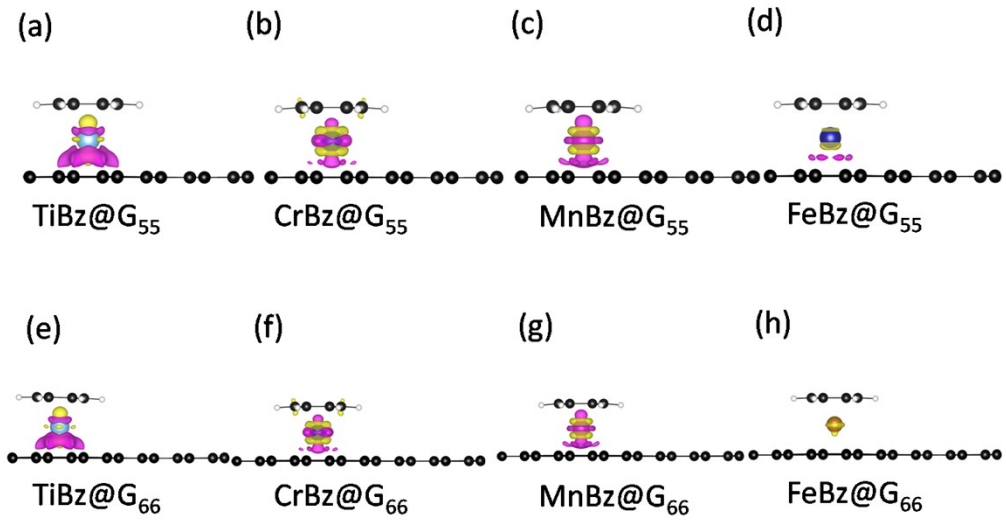

Figure S5.The charge density differences of $TMBz@G_{55}$ and $TMBz@G_{66}$.

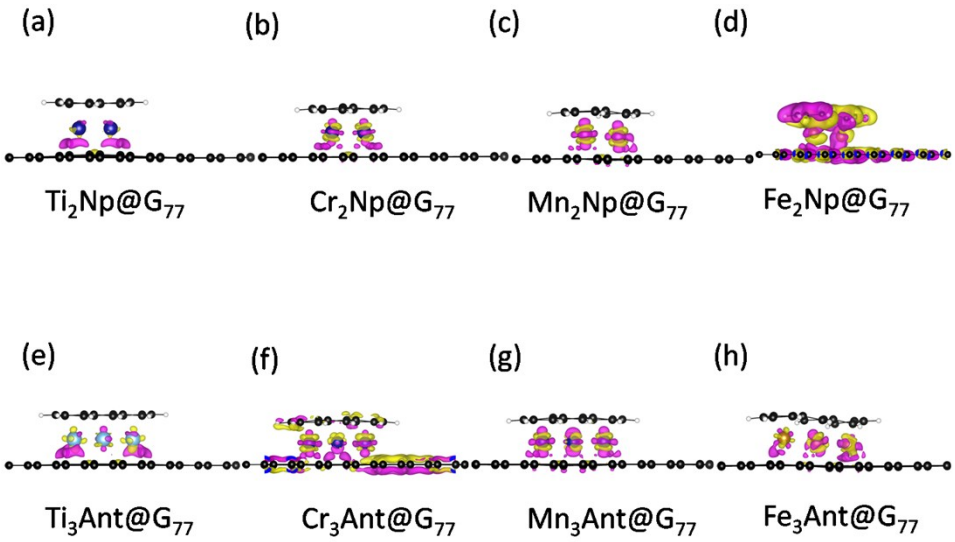

Figure S6.The charge density differences of $TM_2Np@G_{77}$ and $TM_3Ant@G_{77}$.

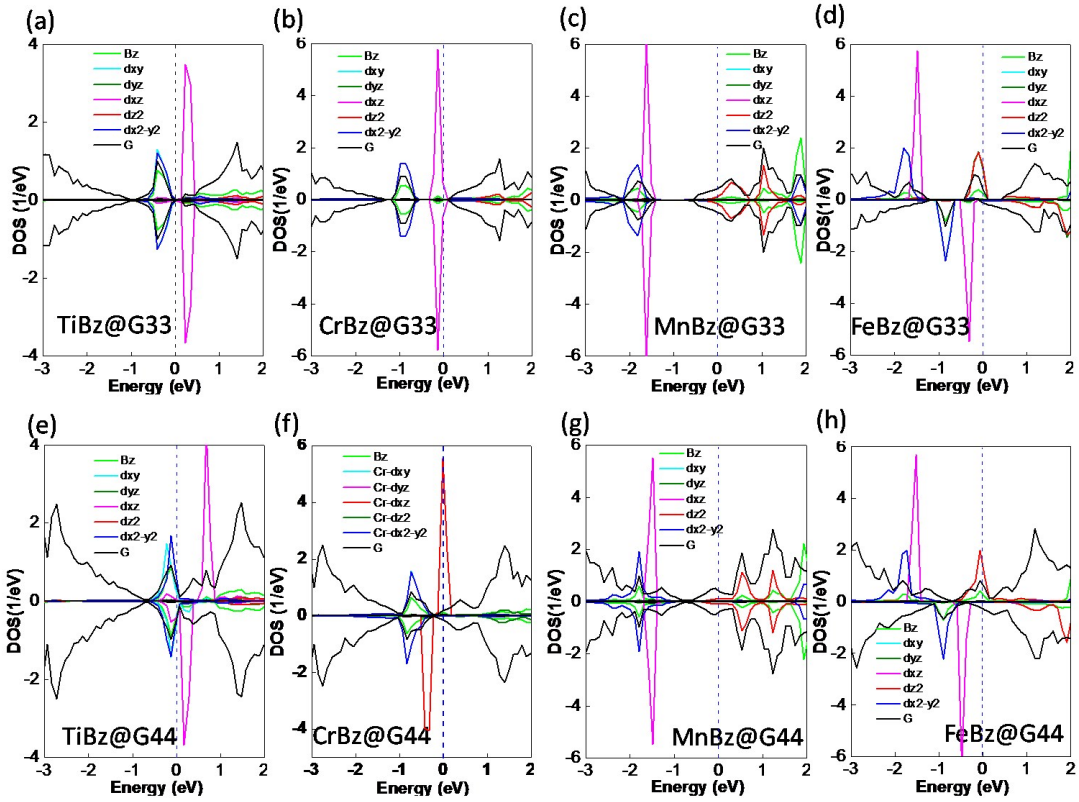

Figure S7.Density of states of of TMBz@G_{33} and TMBz@G_{44}.

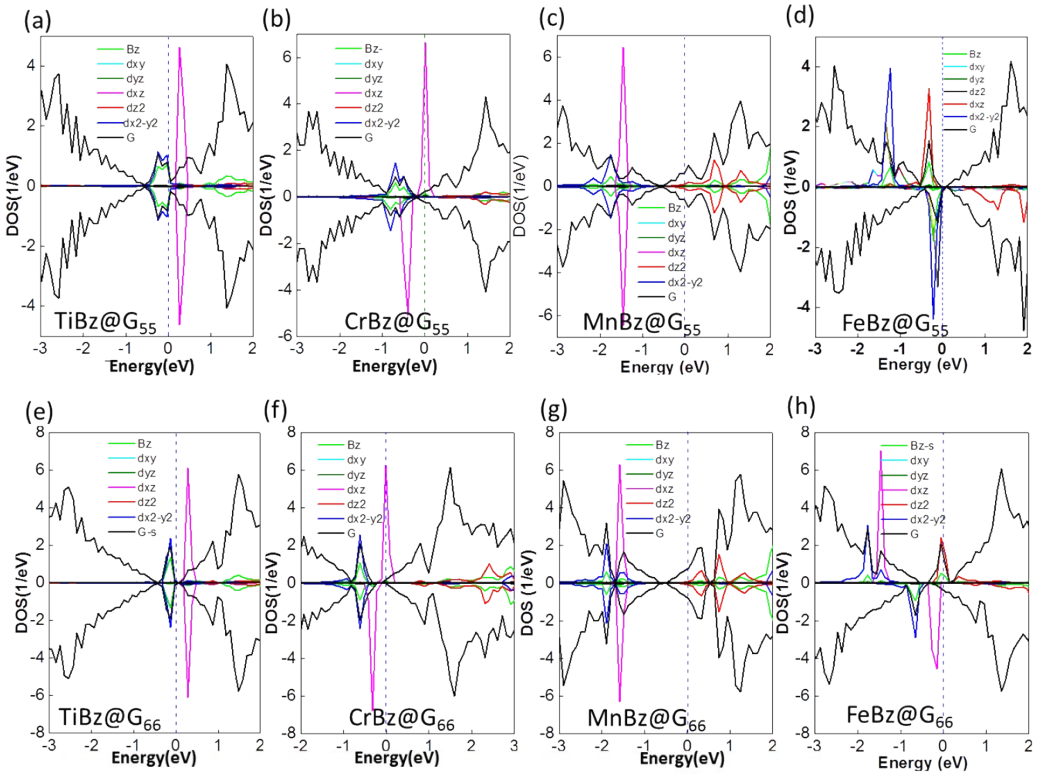

Figure S8.Density of states of of TMBz@G_{55} and TMBz@G_{66}.

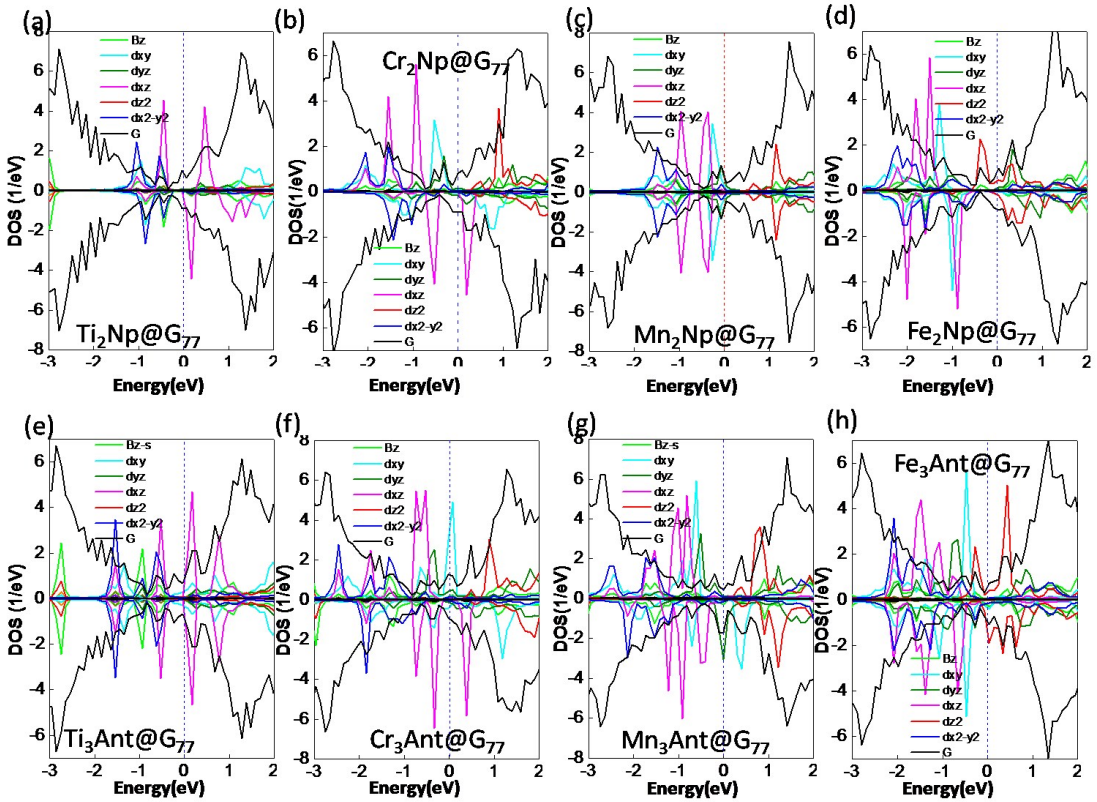

Figure S9.Density of states of of $TM_2Np@G_{77}$ and $TM_3Ant@G_{77}$.

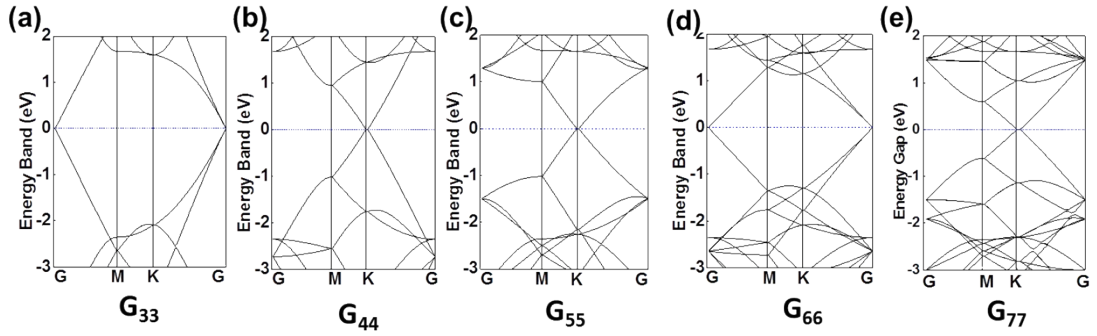

Figure S10. The electronic bandstructures of pristine graphene with different supercell, G_{33}, G_{44}, G_{55}, G_{66}, G_{77}.

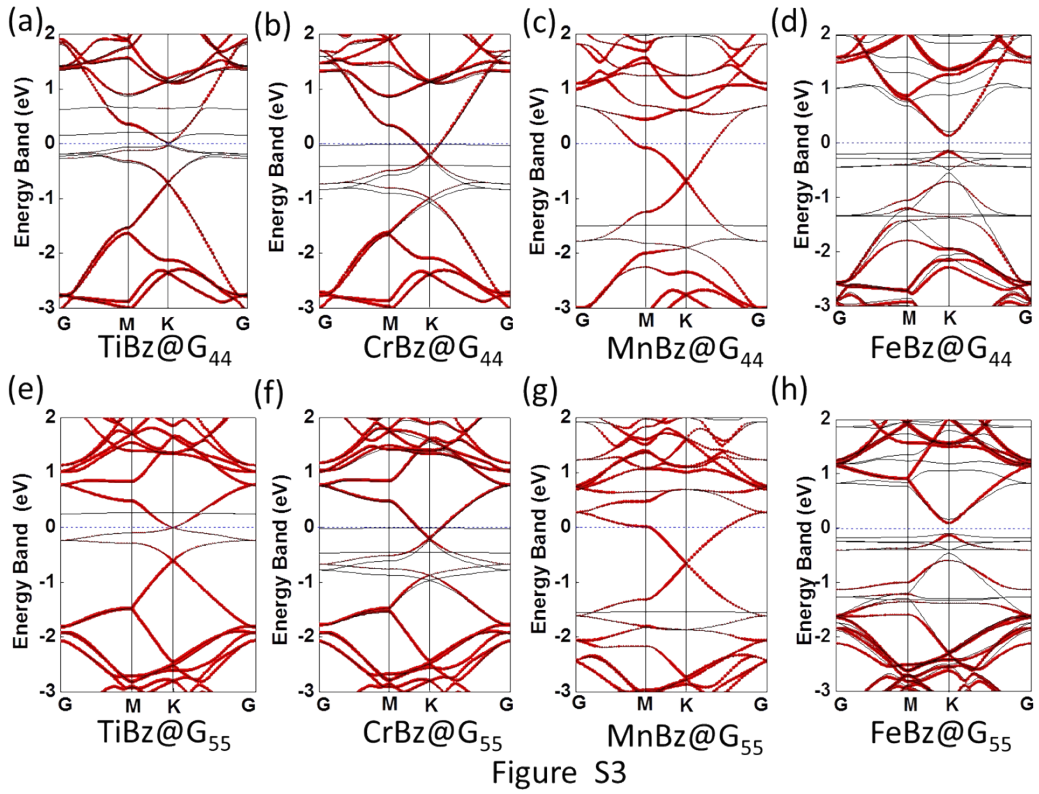

Figure S3

Figure S11. The electronic bandstructures of TMBz@G44 and TMBz@G55.

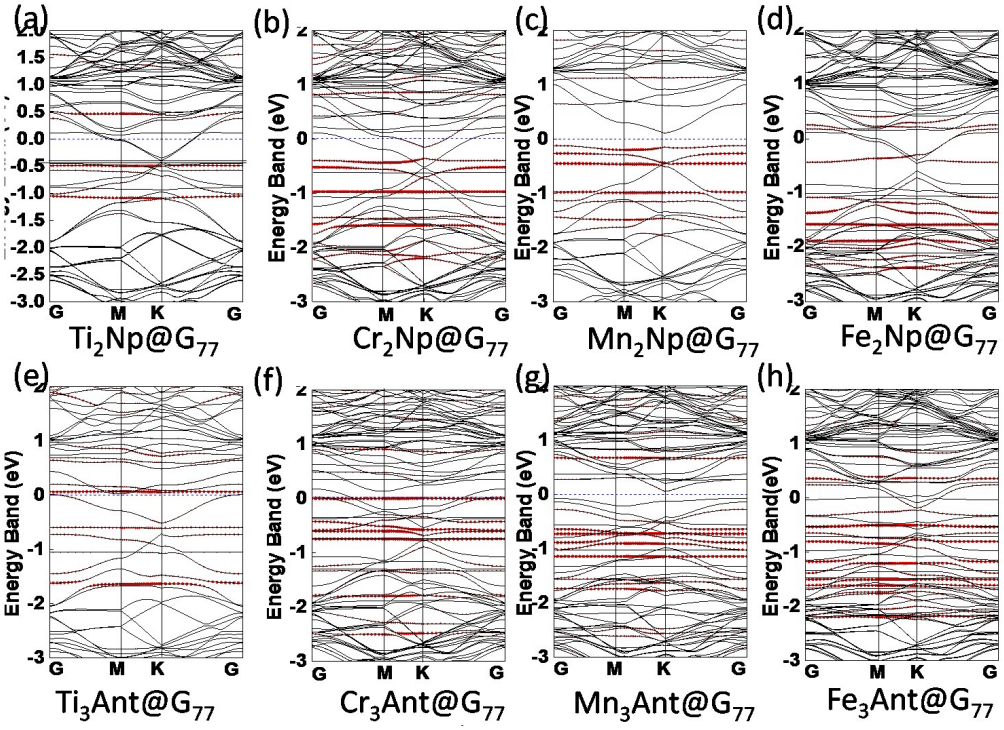

Figure S12. The electronic bandstructures of $TM_2Np@G77$ and $TM_3Ant@G77$.

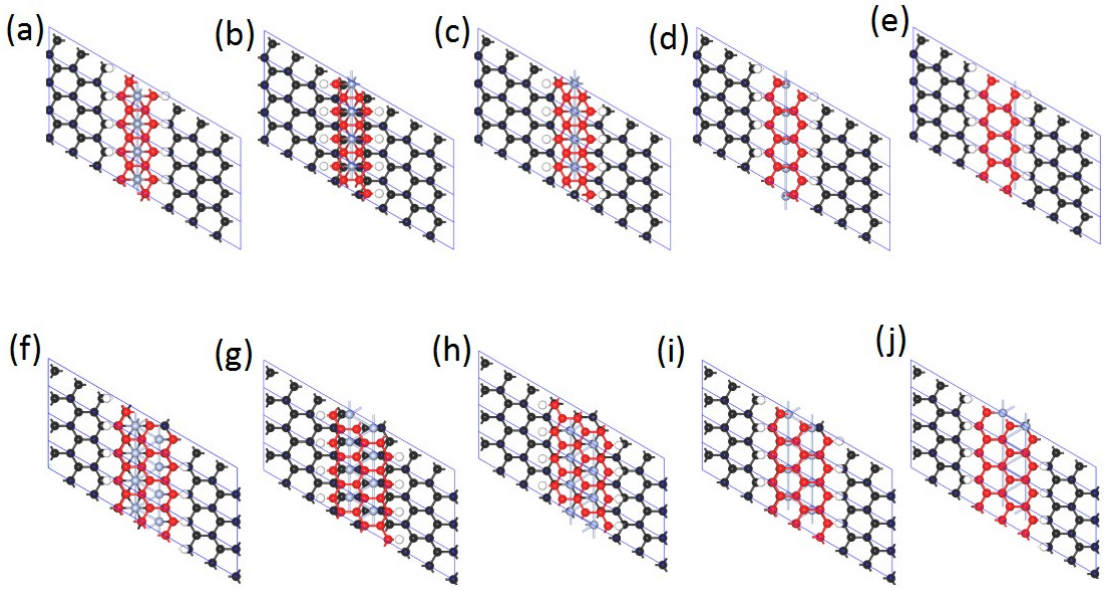

Figure S13. Schematic diagrams of one dimensional $[TMC_4H_2]_\infty$ and $[TMC_6H_2]_\infty$ chains bound on graphene, $[TMC_4H_2]_\infty$@G and $[TMC_6H_2]_\infty$@G: (a, f) HC-HC, (b, g) HC-BR,(c, h) HC-Top, (d, i) BR-BR, (e, j) Top-Top.

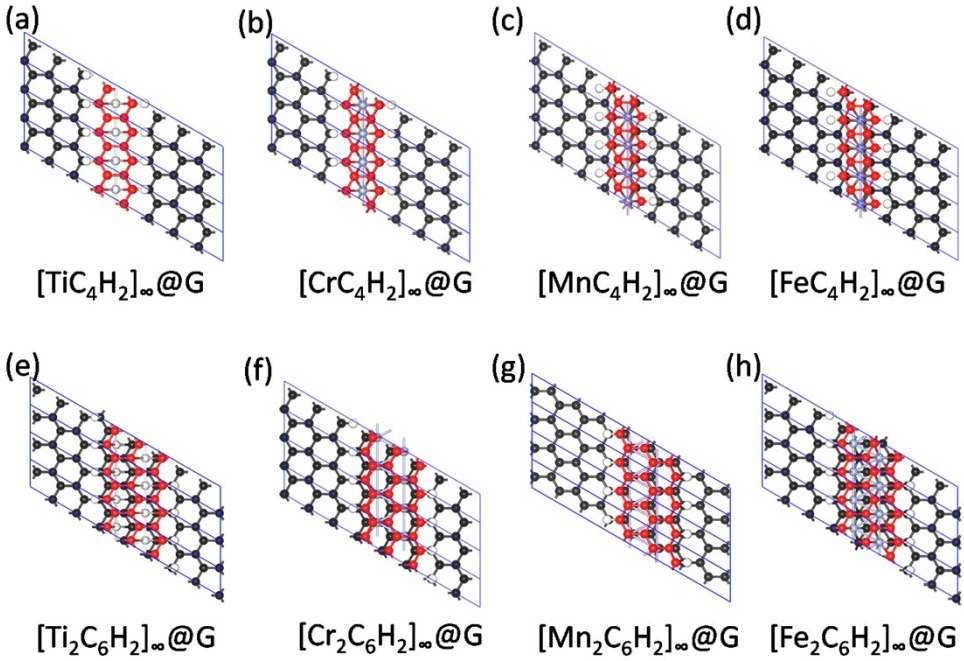

Figure S14. Optimized structures of $[TMC_4H_2]_\infty$ and $[TMC_6H_2]_\infty$.

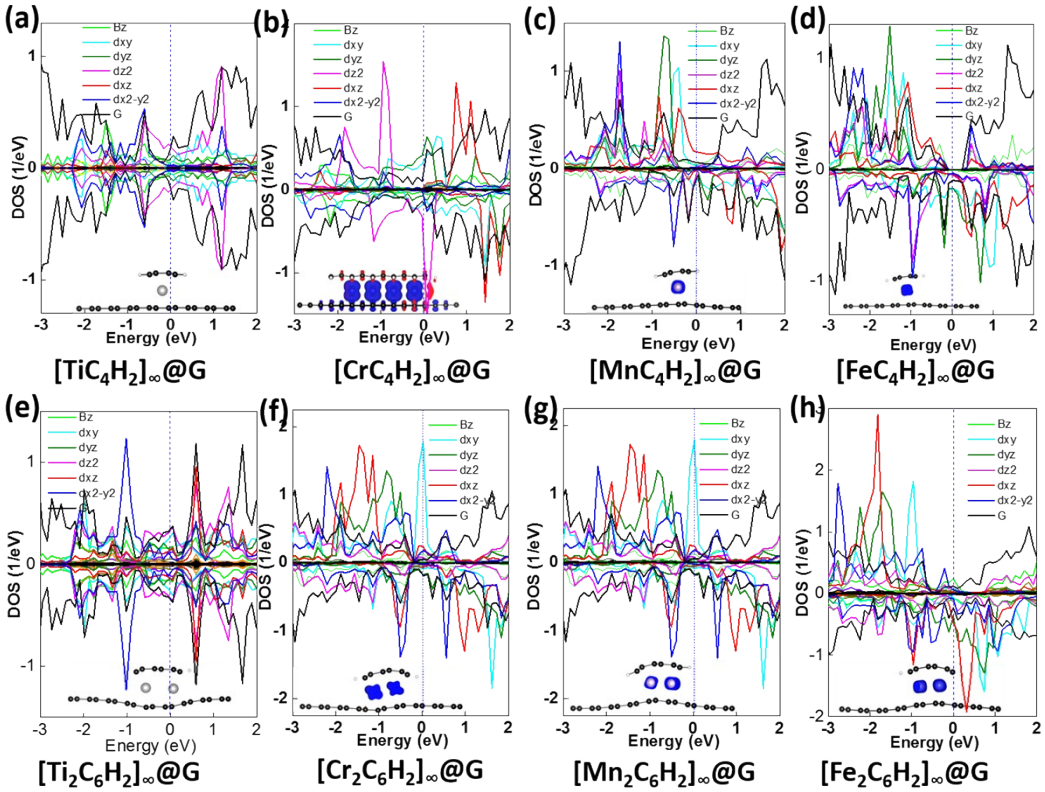

Figure S15. Density of states of (a)-(d) $[TMC_4H_2]_\infty$@G and (e) –(h) $[TMC_6H_2]_\infty$@G, TM=Ti, Cr, Mn, Fe. Insets are the spin density plots of present IFTMOL@SLGs.

Table S2. The systems with infinite adsorbed molecule wires, the C-C bond length of organic ligands ($L_{C\text{-}C(OL)}$) and of graphene ($L_{C\text{-}C(G)}$), the C-H bond lengths of organic ligands ($L_{C\text{-}H}$), the distance of TM atom to the geometric center of organic molecules ($D_{TM\text{-}OM}$) and graphene plane ($D_{TM\text{-}G}$), and the distance of TM-TM ($D_{TM\text{-}TM}$) atoms in IFTMOL@Gs system.

Sys	TM	$L_{C\text{-}C(OM)}$(Å)	$L_{C\text{-}C(G)}$(Å)	$L_{C\text{-}H}$(Å)	$D_{TM\text{-}OM}$(Å)	$D_{TM\text{-}G}$(Å)	$D_{TM\text{-}TM}$(Å)
$[TMC_4H_2]_\infty$@G	Ti	1.425-1.444	1.436-1.438	1.091	1.866	1.929	
	Cr	1.421-1.444	1.423-1.436	1.091	1.739	1.799	
	Mn	1.419-1.448	1.422-1.434	1.091-1.092	1.715	1.748	
	Fe	1.417-1.463	1.425-1.448	1.090	1.755	2.020	
$[TMC_6H_2]_\infty$@G	Ti	1.421-1.456	1.423-1.459	1.892-1.092	2.444,1.892	1.901,2.357	2.950
	Cr	1.421-1.450	1.425-1.446	1.093,1.095	2.206,1.965	2.019,2.126	2.691

Mn	1.426-1.446	1.425-1.465	1.093	2.127,2.067	2.112,2.094	2.643	
Fe	1.421-1.450	1.420-1.445	1.093	2.407,2.365	2.439,2.468	2.455	

Sys	TM	$L_{C-C(OM)}$(Å)	$L_{C-C(G)}$(Å)	L_{C-H}(Å)	D_{TM-OM}(Å)	D_{TM-G}(Å)	D_{TM-TM}(Å)	EG	E_b(eV)	MM(μ_B)
$[TMC_4H_2]_\infty$@G	Ti	1.425-1.444	1.436-1.438	1.091	1.866	1.929		$Ti^{-1.0579}L^{+0.5399}G^{+0.5181}$	-3.75	0.00
	Cr	1.421-1.444	1.423-1.436	1.091	1.739	1.799		$Cr^{-0.8759}L^{+0.4083}G^{+0.4676}$	-0.91	0.83
	Mn	1.419-1.448	1.422-1.434	1.091-1.092	1.715	1.748		$Mn^{-0.77}L^{+0.3408}G^{+0.4293}$	-0.95	2.36
	Fe	1.417-1.463	1.425-1.448	1.090	1.755	2.020		$Fe^{-0.6656}L^{+0.3232}G^{+0.3423}$	-1.92	2.00
$[TMC_6H_2]_\infty$@G	Ti	1.421-1.456	1.423-1.459	1.892-1.092	2.444,1.892	1.901,2.357	2.950	$Ti^{-1.7288}L^{+0.8225}G^{+0.9063}$	-7.97	0.00
	Cr	1.421-1.450	1.425-1.446	1.093,1.095	2.206,1.965	2.019,2.126	2.691	$Cr^{-1.3897}L^{+0.6898}G^{+0.7}$	-3.17	1.28
	Mn	1.426-1.446	1.425-1.465	1.093	2.127,2.067	2.112,2.094	2.643	$Mn^{-1.1672}L^{+0.6228}G^{+0.5444}$	-3.36	5.03
	Fe	1.421-1.450	1.420-1.445	1.093	2.407,2.365	2.439,2.468	2.455	$Fe^{-0.9972}L^{+0.531}G^{+0.4665}$	-5.20	4.4312

Sys	**TM**	**$L_{C-C(OM)}$(Å)**	**$L_{C-C(G)}$(Å)**	**L_{C-H}(Å)**	**D_{TM-OM}(Å)**	**D_{TM-G}(Å)**	**D_{TM-TM}(Å)**	**EG**	**E_b(eV)**	**MM(μ_B)**
[TM@BLG]1:2	Ti	1.426	1.426		1.997	1.996		$Ti^{-0.7469}Bz^{+0.3748}G^{+0.3721}$	-3.27	-0.0001
	Cr	1.426	1.426		2.006	2.005		$Cr^{-0.5544}Bz^{+0.2793}G^{+0.275}$	-0.90	0.5076

	Mn	1.428	1.428		2.503	2.504		$Mn^{-0.3821}Bz^{+0.1889}G^{+0.1932}$	-2.24	1.5261
	Fe	1.426	1.426		5.417	10.089		$Fe^{-0.0058}Bz^{+0.003}G^{+0.0028}$	-3.15	2.8143
2D-TMBz(2)	Ti	1.422	1.422		1.892	1.892		$Ti^{-1.2536}Bz^{+0.6269}G^{+0.6268}$	-3.21	1.2177
	Cr	1.426-1.427	1.426-1.427		1.878	1.878		$Cr^{-1.056}Bz^{+0.5272}G^{+0.5287}$	-0.52	3.5776
	Mn	1.426-1.427	1.426-1.427		1.834	1.834		$Mn^{-0.9752}Bz^{+0.487}G^{+0.4882}$	-0.51	3.0164
	Fe	1.424	1.424		1.700	1.700		$Fe^{-0.7529}Bz^{+0.3773}G^{+0.3756}$	-1.65	1.7234
2D-TMBz(3)	Ti	1.424-1.428	1.424-1.428		1.921	1.922		$Ti^{-1.0363}Bz^{+0.5179}G^{+0.5184}$	-3.74	0.0002
	Cr	1.425-1.434	1.425-1.434		1.124	1.768		$Cr^{-0.8692}Bz^{+0.434}G^{+0.4353}$	-0.91	1.1240
	Mn	1.425-1.435	1.425-1.435		1.739	1.739		$Mn^{-0.744}Bz^{+0.3735}G^{+0.3705}$	-0.81	1.0750
	Fe	1.427-1.431	1.427-1.431		1.856	1.859		$Fe^{-0.647}Bz^{+0.3243}G^{+0.3226}$	-1.73	2.0564
TM2D-double hex	Ti	1.411-1.437	1.411-1.437		1.881 1.881	1.880 1.880	4.452	$Ti^{-2.4949}Bz^{+1.2418}G^{+1.2532}$	-5.79	2.5468
	Cr	1.413-1.432	1.413-4.432		1.804 1.804	1.804 1.804	4.278	$Cr^{-2.1883}Bz^{+1.0848}G^{+1.1035}$	-0.30	5.5959
	Mn	1.413-1.443	1.413-1.443		1.642 1.642	1.644 1.644	4.278	$Mn^{-1.7329}Bz^{+0.8507}G^{+0.882}$	-0.79	0.0001
	Fe	1.414-1.432	1.414-1.432		1.722 1.722	1.722 1.722	4.278	$Fe^{-1.5348}Bz^{+0.7604}G^{+0.77425}$	-2.56	3.7009
TM2D-double hex-2	Ti	1.419-1.452	1.414-1.438	1.083-1.087	1.772	1.847		$Ti^{-1.3455}Bz^{+0.6998}G^{+0.646}$	-2.73	-0.0004
	Cr	1.413-1.458	1.414-1.440	1.084-1.085	1.563	1.718		$Cr^{-0.9476}Bz^{+0.4855}G^{+0.462}$	-0.39	0.0000
	Mn	1.413-1.458	1.419-1.434	1.083-1.085	1.592	1.749		$Mn^{-0.8716}Bz^{+0.3745}G^{+0.4968}$	0.03	0.0094
	Fe	1.412-1.459	1.420-1.433	1.085-1.08	1.680	1.842		$Fe^{-0.767}Bz^{+0.3967}G^{+0.3702}$	-0.80	1.9999

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TM2D-double hex-22	Ti	1.418-1.434	1.418-1.434		1.899	1.899		$Ti^{-}{}^{1.2187}Bz^{+0.5983}G^{+0.6206}$	-3.83	2.3368
	Cr	1.422-1.437	1.422-1.437		2.079	2.064		$Cr^{-}{}^{1.0191}Bz^{+0.5021}G^{+0.5172}$	-1.03	4.4262
	Mn	1.420-1.432	1.420-1.432		1.779	1.778		$Mn^{0.248}Bz^{+0.3563}G^{+0.3956}$	-0.41	-0.0379
	Fe	1.420-1.433	1.420-1.433		1.734	1.734		$Fe^{-}{}^{0.7611}Bz^{+0.3603}G^{+0.4008}$	-1.76	0.0370
TM2D-double hex-hole	Ti	1.415-1.448	1.414-1.441	1.083-1.086	1.826 1.825	1.904 1.903	3.737	$Ti^{-}{}^{2.4413}Bz^{+1.2404}G^{+1.2009}$	-9.02	1.9832
	Cr	1.407-1.453	1.409-1.446	1.082	1.639 1.639	1.663 1.663	4.278	$Cr^{-}{}^{1.8449}Bz^{+0.9062}G^{+0.939}$	-4.03	0.0000
	Mn	1.408-1.438	1.410-1.443	1.083	1.612 1.612	1.663 1.663	4.246	$Mn^{-}{}^{1.7209}Bz^{+0.8275}G^{+0.8935}$	-3.70	0.0000
	Fe	1.407-1.443	1.418-1.430	1.083	1.663 1.662	1.777 1.775	4.293	$Fe^{-}{}^{1.5388}Bz^{+0.7442}G^{+0.7945}$	-5.12	-1.7577